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GHGT-12

A low energy aqueous ammonia CO₂ capture process

Jozsef Gaspar^a, Muhammad Waseem Arshad^a, Eirik Ask Blaker^b, Birger Langseth^b, Tord Hansen^c,
Kaj Thomsen^a, Nicolas von Solms^a, Philip Loldrup Fosbøl^{a,*}

^aTechnical University of Denmark, Department of Chemical Engineering, Center for Energy Resource Engineering, Søltofts Plads, 2800, Kgs. Lyngby, Denmark

^bBilfinger Industrial Services Norway AS, Hydroveien 55, NO-3905 Porsgrunn, Norway

^cSilicaTech, 0411 Oslo, Norway

Abstract

The most pressing challenges regarding the use of ammonia for CO₂ capture are the precipitation limitation and the energy penalty of solvent regeneration. Precipitation-free operation is a vital task since solids may cause the shutdown of the plant. Precipitation and slurry formation can be avoided by increasing temperature and L/G ratio but this leads to higher heat consumption, jeopardizing the economic feasibility.

Here we developed, investigated, and optimized a novel CO₂ capture process design using aqueous ammonia as solvent. The proposed configuration replaces the traditional stripper for solvent based CO₂ capture with a thermal decomposition reactor. The overall energy penalty is reduced at the expense of introducing a solid handling section which consists of a saturation reactor, a crystallizer and a belt filter.

The feasibility of the present approach is demonstrated by simulation. Flow-sheet calculations are performed in Aspen Plus using the extended UNIQUAC thermodynamic model for vapor-liquid-solid equilibria and for thermal properties calculation of the CO₂-NH₃-H₂O system.

The simulation results show that the specific regeneration duty of the novel capture alternative is comparable with existing aqueous ammonia CO₂ capture processes. Moreover, the thermal reactor can operate at 1 bar and 86 °C, therefore the NH₃ regeneration temperature is reduced by approximately 50 °C. The integration of low- and mid- temperature waste heat becomes possible which can greatly improve the economics of the process. The present capture alternative is especially convenient for power plants but is also beneficial for the cement, steel and aluminum industry.

Special attention is given to the ammonia slip prediction. The calculations substantiate that the slip above the absorber is 0.1 mol % after washing with the rich solution and it reduces below 100 ppm by washing with low temperature water.

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Keywords: CO₂ post-combustion capture simulation and optimization; aqueous ammonia; slurry and solid formation; low energy process; extended UNIQUAC

1. Introduction

The great paradox of the 21st century is to meet the increasing global demand for energy and products while simultaneously mitigating the climate change [1]. If both these criteria are to be met, carbon capture and storage is an imperative technology for sustainable energy infrastructure development.

Several capture technologies exist at varying levels of maturity. Post-combustion capture is a so-called “end-of-pipe” technology which is suitable for various processes in power plants, steel industry, cement production, and bio-chemical industry. It is particularly attractive since it can be retrofitted to existing plants.

* Corresponding author. Tel.: +45-45252800; fax: +45-45882258

E-mail address: plf@kt.dtu.dk

Today there is a potential for innovative solvent designs and process configurations. One promising solvent for the CO₂ capture process is ammonia, due to its low cost, limited degradation and fast reaction kinetics. The technical feasibility of the aqueous ammonia CO₂ capture process is proven, meaning that the CO₂ capture percentage can be maintained at 90% with CO₂ purity over 95%. The successful commercialization of ammonia based carbon capture technology narrows down to the economic feasibility optimization. For this, the energy consumption of the regeneration step needs to be lowered. In addition, some technical issues including ammonia slip, precipitation and slurry formation need to be resolved before the technology can be deployed [2].

Several research groups are developing different variants of the of the aqueous ammonia CO₂ capture process to replace the traditional amine-based technology. One of the leading approaches is the chilled ammonia process (CAP) developed by Alstom Power Company [3]. The CAP relies on the exhaust gas treatment with high concentration (~28 wt%) ammonia solution at very low temperatures, preferably below 10 °C. The main issue of the CAP process is the energy consumption associated with cooling and the high ammonia slip and washing plus regeneration of the wash water. It might also suffer from solid precipitation, depending on the process condition. One way to reduce the ammonia slip is to decrease the lean solution ammonia content, for example the CSIRO process which uses ~6wt% NH₃ solution [4,5]. However, low NH₃ concentration results in higher energy consumption for CO₂ stripping respectively ammonia regeneration and much higher electricity cost for circulating the liquid. Moreover, due to high loading and low temperature of the rich solution, precipitation and solid handling is a key challenge for the CSIRO process [2]. A unique CO₂ capture process, using low concentration (~10 wt%) aqueous ammonia solution is the RIST process. This process is optimized for the iron and steel industry. Although it is an energy intensive process, Rhee et al. [6] presented the economic feasibility of the process by recovering low- and mid-temperature waste heat from the boiler stack at 140 – 150 °C.

The design of the above ammonia processes is based on a standard absorption and desorption column. The difference between them relies in the operational conditions, such as different ammonia concentration of the lean solution, the operating temperature range of the absorber and regenerator, and different pressures. All of these technologies face some common technical issues related to the volatile nature of ammonia, the energy intensiveness of gas cooling and solvent regeneration, and finally the risk of clogging of the equipment due to solid precipitation.

In the present work a low energy CO₂ capture process using aqueous ammonia is developed and investigated. This novel alternative addresses the main issues of existing process configurations. The overall energy penalty is reduced at the expense of introducing a solid handling section which consists of a saturation reactor, a crystallizer and a filter. In contrast with the traditional solvent based CO₂ capture, the present configuration is centered on thermal decomposition of a solid.

The feasibility of the process is evaluated by simulation. The plant model is based on the extended UNIQUAC thermodynamic framework which is able to accurately predict vapor-liquid-solid equilibrium (VLSE) in the CO₂-NH₃-H₂O system. This analysis reveals that the regeneration duty is comparable with existing aqueous ammonia capture processes. Special attention is given to the NH₃ slip evaluation. An ethyl-glycol based heat pump is used to maintain the temperature at 2 °C. Simulation suggests that the NH₃ slip is below 100 ppm by washing with CO₂-loaded solution and water, and down to 1 ppm by washing with acid solution.

2. Extended UNIQUAC thermodynamic model for NH₃-CO₂-H₂O system

The extended UNIQUAC thermodynamic model proposed by Thomsen and Rasmussen [7] and upgraded by Darde et al. [8] for NH₃-CO₂-H₂O system is applied in the present work to accurately describe the solid-liquid-vapor equilibria as well as the thermal properties. The phase equilibrium is calculated in a γ - ϕ approach coupled with equilibrium speciation reactions with solid precipitation. Therefore, liquid phase activity coefficients are calculated with the extended UNIQUAC model, and the gas phase fugacity coefficients are estimated with the Soave-Redlick-Kwong equation of state [9], solid phase are assumed to be pure.

Extended UNIQUAC is a Gibbs excess energy model with adjustable parameters to account for the system specific interactions between ions and molecules. These parameters have been found through data reduction by fitting to more than 3700 experimental data points from various types of experiments, such as vapor-liquid equilibrium, solid-liquid equilibrium, enthalpy measurements, speciation data and heat capacity [10]. A description of how parameter fitting is performed and the framework surrounding it is detailed by Thomsen [11]. This model has been implemented in Aspen Plus® commercial simulator using a user model interface, developed by Maribo-Mogensen [8].

The excellent behavior of the extended UNIQUAC model in the NH₃-CO₂-H₂O system for absorption and desorption was demonstrated by Darde et al. [8]. Furthermore, it was compared against the e-NRTL model implemented in Aspen Plus®. The analysis has revealed that the extended UNIQUAC model is valid for the whole loading range up to 150 °C. It performs better than e-NRTL for the system of interest. The study outlines that the partial pressure and solid formation is better estimated using the extended UNIQUAC model. It describes the solid-liquid-vapor equilibria, speciation and thermal properties of the system are well predicted using this model [10]. DTU's version of the extended UNIQUAC Aspen Plus user model is used in the present work for the novel ammonia capture process simulation.

3. A low energy CO₂ capture process

3.1. Description of the process configuration and design specifications

The current study presents a new design for the ammonia based CO₂ capture process which solves the challenge of absorber clogging and simultaneously minimizes the specific energy requirement. The novelty of the process configuration relies in a re-designed solvent regeneration unit and solid handling section. The idea is to decrease the operational temperature in order to enable integration to low- and mid- temperature waste heat. The main units of the CO₂ capture process are detailed in the following. The basic working principle of the process is shown in fig. 1.

First the flue gas is cooled to 30 °C in direct contact coolers (DCC) by the wash water leaving the second wash column, Wash 2. The flue gas is treated using a relatively low ammonia content aqueous solution (~15 wt% NH₃), with a CO₂ loading of approximately 0.3 mol CO₂/mol NH₃. To assure a flexible and precipitation free operation of the absorbers, 65% of the CO₂ is captured in the first absorber and the remaining CO₂, up to 90%, is absorbed in the second column. A kind of intercooling is applied where the bottom exit stream from Absorber 1 is cooled to 10 °C and enters the top of the second absorber. The gas exiting the top of Absorber 1 is cooled to 15-15 °C before it is injected in the bottom of Absorber 2. This configuration allows for maintaining a low temperature at the top of Absorber 2, thus reducing the ammonia slip [10].

It can be seen that Absorber 1 is operated above 20 °C and Absorber 2 above 10 °C, minimizing the risk of clogging. The loading of the rich solution leaving Absorber 1 is approximately 0.35, being operated far from conditions at which solid precipitates. The loading of the liquid exiting Absorber 2 is around 0.53 at 13 °C. To assure the flexibility of operation and to avoid the risk of clogging of Absorber 2, it is recommended to use a bubble column or a packed column with special packing designed for precipitating systems, like a mushroom cap column.

Despite the relatively low NH₃ concentration of the lean solution, the gas exiting from Absorber 2 has a high ammonia content, around 1 wt% NH₃. It needs to be washed before being released to the atmosphere. In the present work three stages washing section is implemented to lower ammonia slip below 2 ppm. In the first stage, the gas stream is contacted with CO₂-loaded solution at 13 °C to reduce the slip to 0.1-0.3 wt%. The remaining ammonia is captured by washing with water at approximately 2 °C and with diluted acid solution, as shown in fig. 1. The washing streams are preliminary chilled before entering the columns. An ethyl-glycol based heat pump is used to maintain the temperature.

Fig. 1 shows that rich solution exiting Absorber 2 is sent to a saturation reactor and crystallizer. The role of the saturation reactor is to load the rich solution with CO₂, to obtain a slurry rich in ammonium bicarbonate. The solid NH₄HCO₃ content of the slurry is maximized in the crystallizer by cooling down to 15 °C with available cooling water. By using filter, the liquid and solid phases of the stream exiting the crystallizer are separated. The slurry flows to the thermal reactor while the liquid phase is contacted with the flue gas from Absorber 2 respectively the CO₂ product stream to reduce the ammonia slip. The slurry from the filter is assumed to be a 70 wt% ammonium bicarbonate slurry. This configuration captures ~80% of the CO₂ in the slurry and therefore the traditional stripper can be replaced by a thermal decomposition reactor, as outlined in fig. 1.

As shown in fig. 1, the thermal reactor in which the solid is decomposed consists of two sections: preheating of the slurry with available process heat and decomposition of the solid ammonium bicarbonate to regenerate the solvent. The optimal decomposition temperature is between 85 and 120 °C, depending on the operating pressure, from 1 to 5 bar. Therefore the CO₂ regeneration temperature can be reduced by approximately 25 to 50 °C. Integration of low- and mid- temperature waste heat becomes possible. This is especially convenient for the cement, steel and aluminum industry but also for power plants. Furthermore, the heat of the liquid stream exiting the washing section and the thermal reactor is recovered by pre-heating the slurry to 65 – 70 °C. Moreover, a small 0.028 GJ/ton CO₂ heat pump is applied in order to assure the constant preheating of the slurry. The preheating is carried out in two heat exchangers, HTX1 and HTX2. In HTX1 the slurry is heated up to 55 – 60 °C by the stream exiting the washing section and in HTX2 the heat of the hot lean stream, exiting the thermal reactor, is recovered. Note that a 10 °C temperature approach is applied in all of the heat exchangers. A gas-liquid separator is included between the two heat exchangers to minimize the risk of cracking of the material due to induced vibrations by evaporation. The gas rich in CO₂ out of the separator is sent to the top of the first wash column while the liquid flows to the core of the thermal reactor. Therefore, the inlet flow to the thermal reactor is reduced, thus less heat is needed for CO₂ evaporation. The liquid stream is further heated in the thermal reactor to evaporate CO₂.

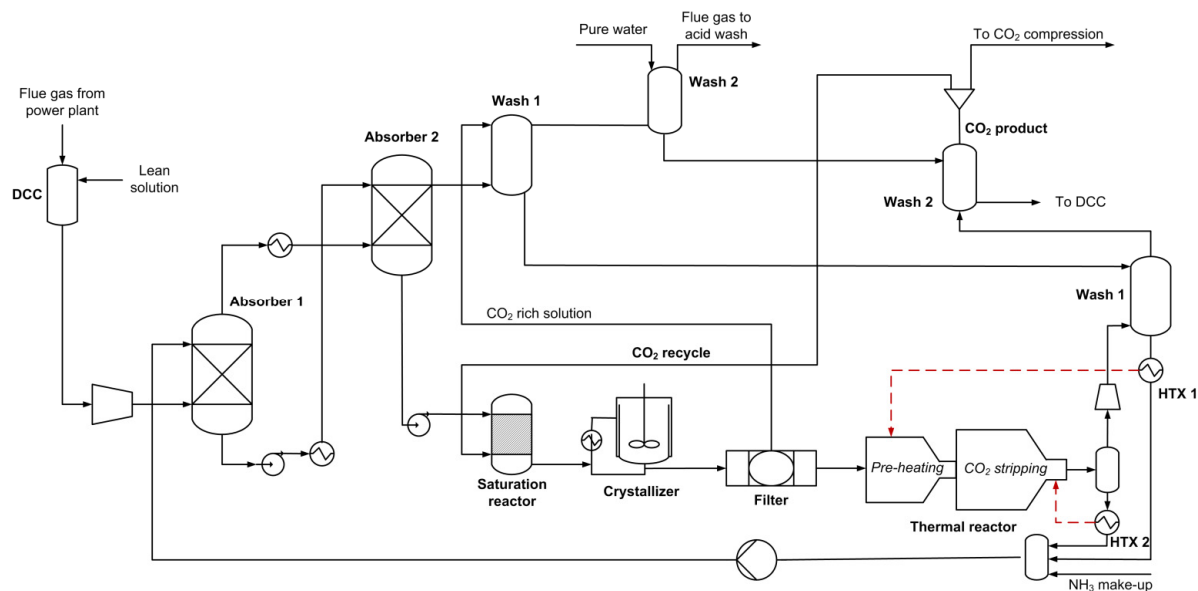


Fig. 1. Schematic of the novel CO₂ capture process

The gas stream exiting the thermal reactor flows through a washing column. Here most of the ammonia is removed by the rich solution from the filter. The cleaning of the product stream is based on the principle that NH_3 dissolves easier than CO_2 in highly loaded solutions. The selectivity of absorption towards ammonia increases exponentially with pressure and temperature. Therefore, it is recommended to operate the washing columns at pressure above 5 bar and above 90 °C to maximize the CO_2 product stream and to avoid precipitation of salts. At these conditions, the gas stream leaving the separation unit has less than 15 wt% NH_3 . The remaining ammonia and traces of water are condensed by washing with water at 30-60 °C. The described methodology can recover 90% of the CO_2 with a purity of 98 wt %.

It can be concluded that the present configuration addresses the burning issues of the existing aqueous ammonia capture processes, such as ammonia slip and risk of equipment clogging and propose a new design to reduce the energy penalty related to CO₂ capture.

3.2. Description of the modeling methodology

The feasibility of the described process configuration is evaluated and demonstrated by means of process simulation. The simulation is equilibrium-based and it is carried out similar to the methodology described by Darde et al. [8] using the extended UNIQUAC thermodynamic model in Aspen Plus.

The absorber and the thermal reactor are modeled as multi-stage equilibrium units. Yu et al. [4] outlined that process simulation models over-predicts the CO₂ absorption rate with more than 15 %. Therefore, an efficiency factor is used in order to obtain results that are closer to real capture plants. This efficiency factor is tuned based on the experimental campaign performed at Bilfinger BIS site in Porsgrunn, Norway.

The solid handling units, the saturation reactor and crystallizer, are setup as TP-flashes. The simulation of the filter is setup to mimic a given efficiency. For example, 70 % efficiency indicates that the slurry contains 70 wt % solid ammonium carbonate in equilibrium with the liquid phase. It is assumed that the crystallizer can be operated at 15 °C using cooling water at 10 °C, using Norwegian summer conditions.

4. Simulation results

The present study evaluates and optimizes the performance of the developed ammonia capture process using a flue gas specific for aluminum-, steel- industry, and natural gas fired power plants. It focuses on important issues related to ammonia based CO₂ capture, namely ammonia slip evaluation, solid precipitation and heat consumption analysis with respect to operating pressure and temperature. The simulation results are shown in fig. 2 to 7. The inlet process parameters and main design specifications used in this study are summarized in table 1.

Table 1. Process parameters for the base case scenario and main design specifications.

Inlet process parameters for the base case	
Flue gas flow rate	2448.2 t/hr
Flue gas inlet temperature	30 °C
Flue gas inlet CO ₂ mol fraction	3.90 %
Lean solvent flow rate	1667.0 t/hr
Lean solvent inlet temperature	26 °C
Ammonia inlet concentration	15 wt%
Design specifications	
Capture rate	90 %
Rich loading	0.55
Ammonia slip	< 1 ppm
Slurry solid mass fraction	70 wt %
CO ₂ product stream purity	> 98 wt%
Cooling water temperature	10 °C
Crystallizer operation temperature	15 °C
Temperature approach for heat exchangers	10 °C

The simulation case corresponds to a 130 t/hr CO₂ capacity post-combustion capture plant using a 15 wt % aqueous ammonia solution. The gas stream is fixed and the CO₂ lean solution flow rate is modeled to capture 90 %. The inlet temperature of the solvent and flue gas is 30 °C and 26 °C, respectively. In addition, the design specifications are specified for the ammonia slip and the CO₂ product stream purity, as shown in table 1. It is considered that the cooling water is available at 10 °C. Note that this value is commonly used in literature.

4.1. Optimization of slurry formation

The focus is on selecting the optimal CO₂ recycle flow for the saturation reactor and the operating temperature for the crystallizer to minimize the heat consumption of the overall process. It is desirable to run these units at atmospheric pressure to lower the CAPEX. To optimize the saturation reactor, the CO₂ recycle is varied between 100 and 300 t/hr and the solid formation is calculated as function of temperature. The equilibrium pressure and specific cooling duty is determined. The results are shown in fig 2 and fig. 3.

Fig. 2 presents the amount of solid and equilibrium pressure as function of the recycle CO₂ flow. It can be seen how solid formation as well as the equilibrium pressure increases if more CO₂ is added. An exponential increase in pressure can be observed above 225 t/hr CO₂. The maximum is reached at 242 to 257 t/hr CO₂ corresponding to 2.7 – 7.5 bar, depending on the operating temperature. This figure also substantiates that the equilibrium pressure exceeds 1 bar above 35 °C for any CO₂ flow. It has to be mentioned that the equilibrium pressure curve represent the minimal pressure value at which CO₂ and NH₃ evaporate, Therefore it is recommended to operate the saturation reactor below 35 °C and with a recycle flow less than 175 t/hr to diminish the loss of CO₂ and NH₃. The figure also substantiates how less solid forms at higher temperatures.

It has to be mentioned that the optimal CO₂ recycle flow does not correspond to the peak of the solid curves. More solid means greater CO₂ recycle flow, as shown in fig. 2, and therefore higher heat duty of the thermal reactor. The CO₂ flow must be minimal but high enough to produce the necessary amount of ammonium carbonate slurry to maintain the plant at 90% CO₂ recovery percentage. Therefore, the lower limit of the recycle flow rate can be estimated by assuming that the CO₂, resulted from the decomposition of the solid, can be recovered completely. In this case, CO₂ in solid and liquid phase has to equal the amount of captured CO₂ from the flue gas, 130 t/hr, plus the CO₂ recycle flow. Based on fig. 2, it can be seen that at least 130 t/hr CO₂ needs to be recycled to the saturation unit, which corresponds to a solid production of 310 – 450 t/hr, depending on the temperature. Therefore, it can be concluded that the saturation reactor should be operated below 35 °C and at 1 bar with a CO₂ recycle flow between 130 and 175 t/hr.

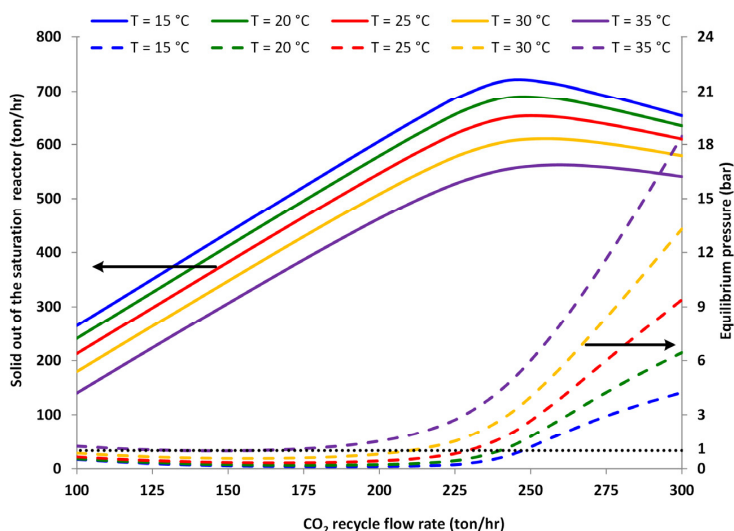


Fig. 2. Effect of CO₂ recycle flow rate on the solid precipitation at different temperatures

Figure 3 shows the sum of the specific cooling duty for the saturation reactor and the crystallizer, when the saturation reactor is operated at 30 °C with a CO₂ recycle flow rate of 140 t/hr. A 5 °C temperature approach is assumed for the crystallizer heat duty calculation. Hence, the crystallizer is cooled down to 15 °C using cooling water at 10 °C and it is chilled to 10 °C using chilled water at 5 °C. Therefore, the isotherms below 15 °C are determined by adding the cooling duty.

Figure 3 highlights that the solid production of the crystallizer and the cooling duty decreases almost linearly with temperature. When the temperature is lowered from 20 to 5 °C at a CO₂ flow rate of 140 t/hr, the amount of precipitated solid decreases from 498 t/hr to 434 t/hr while the specific cooling duty from 0.98 to 0.84 GJ/ton solid. This figure clearly shows that it is expensive to run the process at 5 °C since the effect of temperature on the cooling duty is more pronounced than on the solid formation, especially at temperatures below 13 °C. There is a tradeoff between maximizing solid formation and minimizing the cooling duty. In the present study, the temperature of the crystallizer is set to 15 °C to eliminate the need for an additional chilling unit.

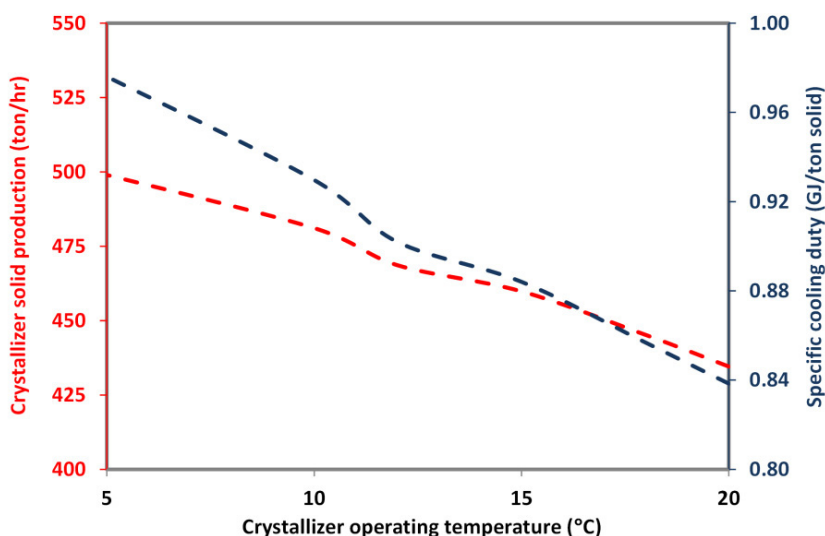


Fig. 3. Specific cooling duty of the crystallizer at different temperatures

It can be concluded that theoretically it is possible to precipitate enough CO_2 to reach a 90% overall CO_2 capture percentage, even at temperatures higher than 15 °C. Therefore, there is no need for chilling towers.

4.2. Optimization of the energy consumption

An analysis of the thermal reactor is performed to investigate the influence of temperature and pressure on the overall process performance. For this, the CO_2 recovery, the lean loading out of the thermal reactor and the solvent regeneration heat duty are calculated at various temperatures and pressures. This study is performed with a CO_2 recycle flow of 140 t/hr and the slurry is cooled down to 15 °C in the crystallizer. The results are shown in fig. 4 and fig. 5.

Figure 4a outlines the influence of pressure and temperature of the thermal reactor on the overall CO_2 recovery. The CO_2 recovery gives the percentage of CO_2 in the product stream sent to compression relative to the absorber inlet CO_2 . The results in fig. 4a show the exponential increase of the recovery percentage with temperature, up to approximately 90%, independent of pressure. However, additional heating of the thermal reactor has no effect on the recovery rate due to higher ammonia evaporation. Fig. 4a demonstrates that the recovery rate of the post-combustion capture plant cannot be further improved by increasing neither the pressure nor the temperature. Even more, when the thermal reactor is operated above 1 bar, the regeneration temperature must be increased without improving the performance. Conclusively it is not beneficial to run the thermal reactor above 1 bar, since the maximum CO_2 production remains the same.

Based on the findings in fig. 4a, the thermal reactor can be operated at 86 °C and 1 bar. Recall that the waste heat, recovered from a boiler stack at 140-150 °C, would successfully supply the heat for the current post-combustion plant. If enough waste heat is available, the energy penalty of the capture unit will drop significantly.

The same conclusion can be reached by analyzing fig. 4b. It shows the loading of the CO_2 -lean stream exiting the thermal reactor as function of temperature at pressures between 1 and 5 bar. A linear dependency of the loading is found as function of temperature. It can be seen, comparing fig. 4a and 4b, that 90 % overall recovery corresponds to a CO_2 loading of 0.23 mol CO_2 /mol NH_3 , independent of the operating pressure. Moreover, it can be concluded that it is not beneficial to go below 0.23 in loading since it reduces the overall performance of the plant.

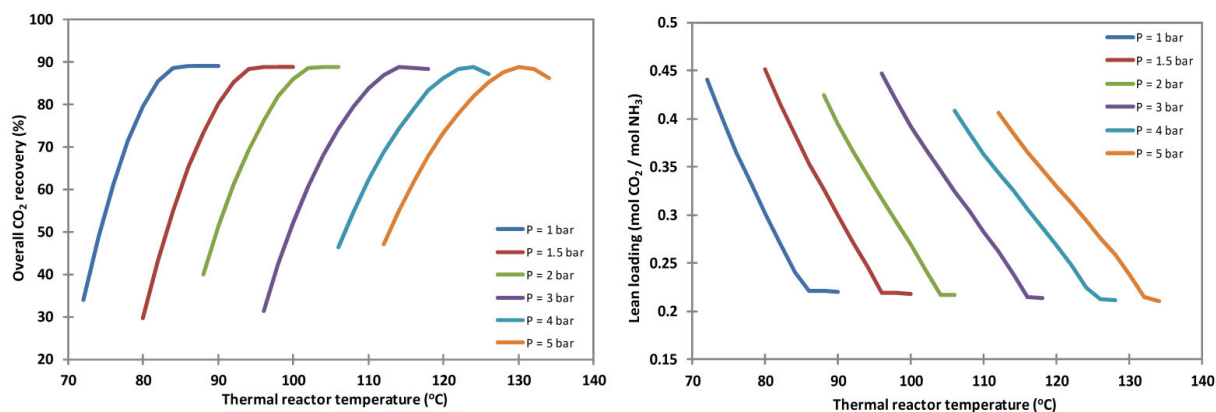


Fig. 4. Influence of temperature and pressure on the (a) overall CO_2 recovery percentage and (b) lean loading after the thermal reactor

Figure 5 presents the specific heat duty of the thermal reactor for several pressure and temperature conditions. Generally the heat duty increases exponentially with temperature from 2.7 to 4.8 GJ/ton CO_2 . The minimum of the heat consumption corresponds to an overall CO_2 recovery percentage between 50% and 75%, depending on the pressure. It can be seen that the same heat duty can be reached at different pressures by varying the temperature.

The CO_2 recovery rate must be kept at 90% at the expense of higher energy consumption. Therefore, the thermal reactor will be run at 1 bar and 86 °C which corresponds to 90% CO_2 recovery and a specific heat duty relative to the product stream of 2.85 GJ/ton CO_2 . These conditions will give a CO_2 product stream with 98 wt% purity.

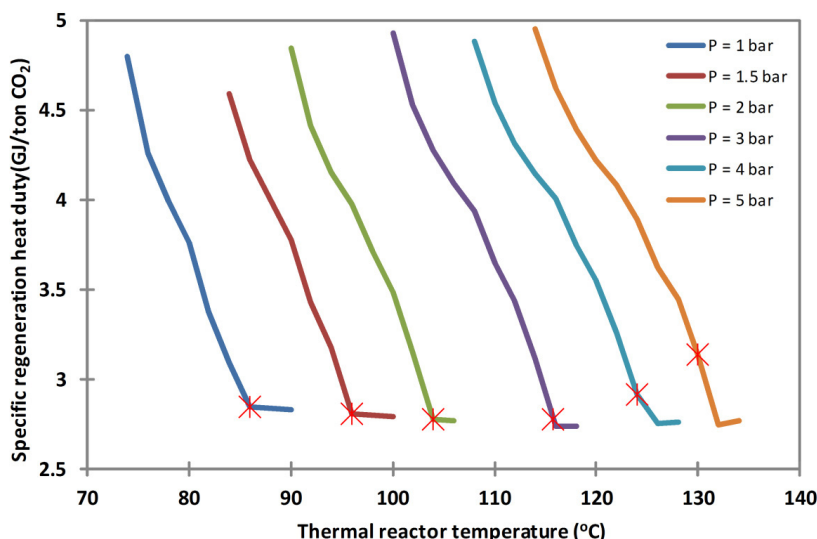


Fig. 5. Influence of temperature and pressure on the specific regeneration energy. Stars correspond to 90 % CO₂ recovery percentage.

The present simulation results substantiates that the novel process configuration has a specific heat duty of the thermal reactor in the order of 2.85 GJ/ton CO₂. Moreover, it demonstrates that the thermal reactor can be run at 1 bar. The analysis reveals that it is not beneficial to run the thermal reactor above atmospheric pressure which would negatively impact the temperature without decreasing the energy consumption. Hence, the process is run at 86 °C and 1 bar allowing the reuse of low-pressure steam and waste heat from the stack.

4.3. Ammonia slip evaluation

This section presents the simulation of the washing section of the aqueous ammonia CO₂ capture process. The capture plant is equipped with two washing sections to reduce the ammonia slip above the absorber and to clean the CO₂ product stream. In both cases, the cleaning of the gas streams takes place in two stages. The first column aims to capture most of NH₃ while the second column is for polishing, as shown in fig. 1. This work shows the ammonia slip calculated at various washing water flow rates and optimizes the operating temperature of the washing columns. The simulation results are shown in fig. 6 and fig. 7.

Fig. 6 presents the ammonia slip above the absorber, after the polishing wash-column at 2, 5 and 8 °C for water flow rates between 100 and 900 t/hr. Note that the wash water contains residue of CO₂ and NH₃ since it is circulated in a closed loop through the DCCs. The aim of the polishing column is to reduce the slip from 0.1 % to less than 100 ppm. Note that the NH₃ content of the gas exiting Absorber 2 is reduced to 0.1 % by washing with the liquid from the filter, in the first wash column. In the simulations, the first wash column is operated at 13 °C.

Fig. 6 shows that the slip drops suddenly from 441 to 143 ppm when the water flow is increased from 100 to 338 t/hr when operated at 2 °C. The same trend of the curve can be seen in fig. 6 for higher temperature values, 5 and 8 °C. Furthermore, the figure substantiates that the water flow must be increased pronouncedly, from 338 t/hr to 595 t/hr, to reduce the slip from 143 ppm to 98 ppm. Further increase of the water flow rate has a minor effect on the ammonia slip, for example a wash water flow of 900 t/hr lowers the slip only to 92 ppm. One might note, in fig. 6, the increase of the operating temperature moves up the curves. Moreover, the slip above the absorber cannot be reduced below 100 ppm of the second stage is operated at greater temperature than 3 °C.

The sensitivity analyses of the polishing unit with respect to water flow rate and temperature showed the benefits of washing at low temperature. In this study, the temperature is set to 2 °C and 580 t/h water is used to reduce the ammonia slip of the sweet gas to 100 ppm.

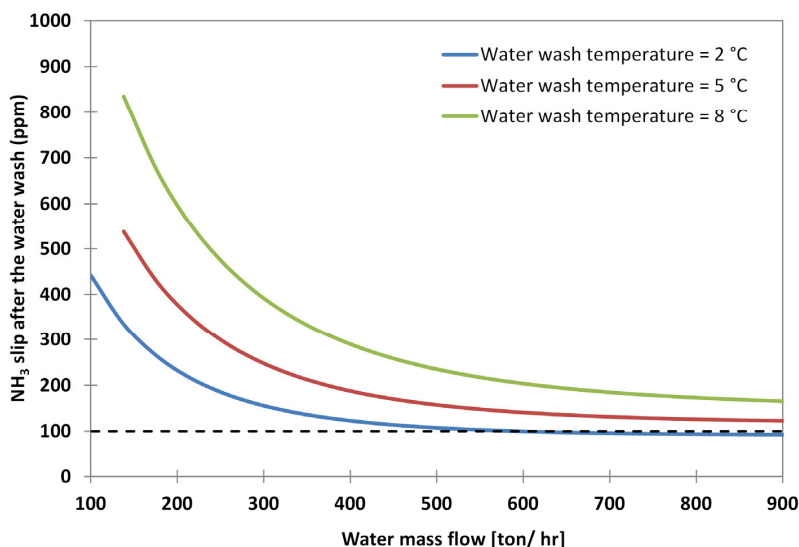
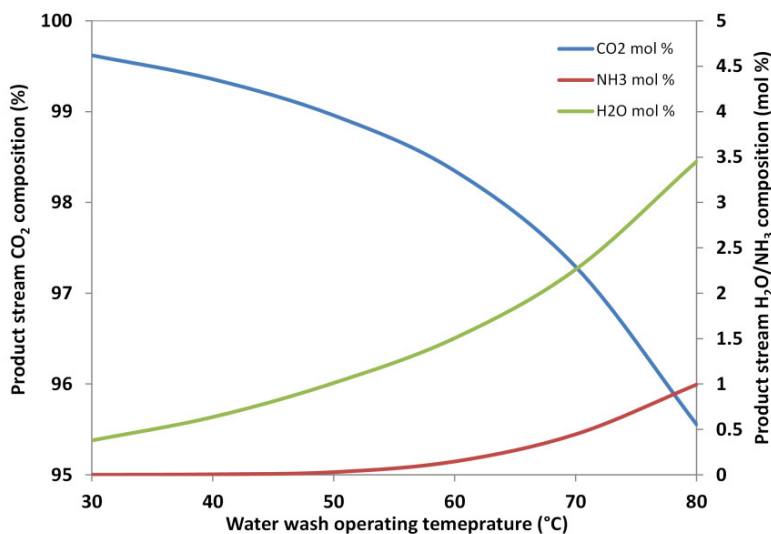


Fig. 6. Ammonia slip versus wash water flow rate

Fig. 7 shows the change in the composition of the pure CO₂ product stream with the washing water flow rate. The figure presents the result of the desorber water wash section when the gas stream exiting the thermal reactor is first contacted with CO₂-rich solution at 12 bar. Note that the ammonia concentration of the gas stream above the thermal reactor is reduced from 40 to 12 wt % in the first wash column, fig. 1.

The temperature of the column determines the purity of the CO₂ product stream, as shown in fig. 7. One might note that the CO₂ fraction decreases while the NH₃ and H₂O content of the gas stream increases with temperature. 98 % CO₂ purity is obtained below 65 °C washing. At this temperature the NH₃ and H₂O concentrations are 0.5 and 1.9 mol % respectively. However, the loss of ammonia can be further reduced at the expense of a higher cooling duty, eg. 10 ppm at 30 °C.

Fig. 7. Composition of the CO₂ product stream as function of temperature at 12 bar

In conclusion, it was demonstrated that the NH_3 composition of the gas stream from Absorber 2 can be reduced from 3.5 wt % NH_3 to less than 100 ppm by washing with the CO_2 -loaded solution from the filter and with water. The calculations demonstrate that 98 % CO_2 purity is reached when the stream is washed with 72 t/hr water at 65 °C and 12 bar. At these conditions the NH_3 slip is 0.15 mol %. The ammonia slip decreases to 10 ppm when the wash column is operated at 30 °C.

5. Conclusions

A low energy aqueous ammonia CO_2 capture process was developed and optimized in the present work. The process has been simulated in Aspen Plus using the extended UNIQUAC thermodynamic model for solid-liquid-vapor equilibria and thermal properties estimation. The flow sheet calculations substantiated that it is beneficial to replace the traditional solvent based stripper with a thermal decomposition reactor. This approach reduces not only the regeneration energy but also the operating temperature. Therefore, waste heat can be recovered which significantly improves the economic feasibility of the process.

The simulation study of a 130 t/hr CO_2 capture plant was performed and optimized. The study has shown that the energy consumption of the developed capture alternative is comparable with existing ammonia based capture processes and therefore it is much lower than the base case MEA solvent. Moreover, it was demonstrated that 90% capture can be achieved using a 15 wt % NH_3 solvent even when the absorber is operated above 10 °C. A thermodynamic analysis reveals that the slip can be lowered to 100 ppm when washed with CO_2 loaded solution and water.

The results showed that 80% of CO_2 can be retained in the solid phase by recirculating pure CO_2 . Therefore, the solvent based stripper can be replaced by a thermal reactor at the expense of a saturation reactor, crystallizer and filter. Note that the decomposition temperature of ammonium bicarbonate is around 73 °C at 1 bar. However, the study shows that the optimal temperature for the thermal reactor is higher, 86 °C, due to humidity of the slurry. At these conditions, 86 °C and 1 bar, the heat duty of the thermal reactor is 2.85 GJ/ton CO_2 . However, the NH_3 regeneration temperature is reduced by approximately 50 °C and therefore low-heat thermal energy can be applied for the heat of the regeneration unit, which will be a substitute for the low pressure steam from the steam turbines. Thus, it will reduce significantly the energy penalty of the capture process.

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